

case of polymers, are highly interesting as they facilitate the irradiation of semiconductor particles. These materials are currently being object of numerous studies to be used as a support for photocatalysts of different nature, in spite of their difficulties due to properties such as high thermal sensitivity and low resistance to photodegradation. It is important to highlight that, as well as ultraviolet radiation, the presence of oxygen and water is also necessary (as a source of hydroxyl anions and protons) in order for the photocatalytic process to take place.

[0012] Therefore, it is necessary for photocatalytic materials to be in a medium complying with these three requirements for its correct activity.

Background on Methods Used to Obtain Photocatalytic Coatings.

[0013] One of the most widely used methods to obtain photocatalytic coatings on different substrates by means of sol-gel methodology is the on-site synthesis of TiO₂ coating. This sol-gel method consists of the hydrolysis and condensation of the organometallic precursors (titanium isopropoxide, titanium tetrachloride, et cetera) followed by the deposition through dip-coating, spin-coating . . . of the coating obtained on the substrate to be coated. With this synthetic methodology, the nature of the initially obtained coatings is usually amorphous (a mixture of several structures or phases) and requires a subsequent calcination phase at around 500-600 C for several hours, in order for the titanium oxide coating to have a major anatase phase, which is the most photoactive crystalline structure of TiO₂. This path has the disadvantage that coatings undergo high-temperature thermal treatments, and coating materials must withstand these conditions.

[0014] Therefore, at the end of the eighties (Takahashi, Y.; Matsuoka, Y. J. Mater. Sci. 1988, 23, 2259) one of the first syntheses of TiO₂ coatings was developed, also basing on this on-site methodology. In order to so, diethanolamine (DEA) was used to control the titanium precursor (titanium isopropoxide) hydrolysis phase when water is added. The presence of ethanolamine in the solution gives rise to stabilizing chelates, which react with metal alkoxides through the alcohol exchange reaction. Other stabilizing chelating agents have been used, such as inorganic and organic acids, although these agents may cause acid corrosion on metal substrates. Acetylacetone, which provides stable soles with near neutral pH, has also been used in order to produce coatings on any substrate. All of these on-site synthesis methods required very high thermal treatments in order to obtain the anatase phase and achieve a good adherence to the substrate.

[0015] Other synthetic methods have been developed in order to obtain photocatalytic coatings with titanium dioxide, in which TiO₂ nanoparticles are initially synthesized and later placed on the substrate, therefore avoiding thermal treatments and obtaining TiO₂ nanoparticle coatings (anatase phase), synthesized through hydrolysis in the aqueous medium of titanium tetrakis (isopropoxide), (Peiró, A. M. et al. Appl. Catal. B-Environ. 2001, 30, 359-373).

[0016] A highly common methodology to obtain coatings using previously synthesized nanoparticles is layer-by-layer deposition. This is how photocatalytic coatings have been developed on PET substrates, basing on the assembling of different layers from suspension nanoparticles with opposite charge. With this methodology, coatings on substrates sen-

sitive to high temperatures, such as metals, textiles, PET . . . can be obtained, as high-temperature thermal treatments are no longer required after deposition in order to induce TiO₂ crystallinity (Sanchez, B. et al. Appl. Catal. B-Environ. 2006, 66, 295). However, it is worth highlighting that electrostatic interaction amongst layers may occasionally not be enough (to create a proper adherence). In such a way that, considering all the disadvantages of the previously described synthetic methods, in recent years new techniques based on sol-gel synthesis of inorganic-organic hybrids have been developed in order to obtain photocatalytic coatings.

[0017] Patent WO 2010/122182 has recently proposed a method in order to obtain hybrid photocatalytic coatings through the sol-gel method in soft synthesis conditions, from a specific percentage of crystalline commercial TiO₂ nanoparticles in anatase phase by means of using a polyether-amine-type catalyst.

[0018] Surprisingly, it has now been discovered that by using a completely different catalyst consisting of inorganic oxide nanoparticles, such as silicon oxide or titanium oxide previously functionalized with certain functional groups, alternative photocatalytic coatings can be obtained on various substrates, metal or of other kind, also in soft synthesis conditions.

[0019] On the possible uses of this type of materials, a wide range of practical applications, all targeting the use of these coatings for anti-corrosion or environmental purposes, is being discovered. Patent WO 1998/32473 already specified the use of this type of coatings as possible absorption filters of environment volatiles through the use of additives. More recently, patent US 1996/5571359 specifies methods for the preparation of photocurable inks and pigments basing on titanium dioxide, and patent US 2006/7144840 B2 mentions procedures and coatings basing on TiO₂ crystals, their physical-chemical properties and their field of applications. Also in patent EP 2001/1069950 B1, a different photocatalytic composition is proposed, obtained by adding commercial TiO₂ nanoparticles to a commercial aqueous colloidal silicon dioxide dispersion for its possible use as paint or filter coating. In patent US 2007/0166467 A1, its application on TiO₂ coatings with a silane base resistant to corrosion in construction materials was proposed. Finally, it is worth highlighting patent ES 2285868 T3 when referring to the possible use of photocurable paints for glass through the use of this type of coatings.

[0020] To sum up, as shown in the state of the art of this patent, regarding heterogeneous catalysis and, more specifically, photocatalytic coatings, there is an actual growing need by industry and society to obtain new materials alternative to the already existing ones, which improve the current photocatalytic properties and are economically competitive and environmentally friendly.

[0021] Furthermore, in their preparation process they will have good adherence to substrates, without high-temperature thermal treatments (which significantly reduces the amount of substrates), in order to obtain a greater universality in their application to substrates in different industrial processes and coating processes.

[0022] The physical-chemical principle for all the aforementioned uses is the same: heterogeneous photochemical reactions catalyzed on the surface in the presence of ultraviolet radiation. In order to better describe this type of reactions, it is necessary to describe in further detail its different components: